April 24, 1884.

THE PRESIDENT in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

Professor Leopold Kronecker, Foreign Member, was admitted into the Society.

The following Papers were read:—

I. "On the Relation between the Electrical Qualities and the Chemical Composition of Glass and Allied Substances." Part I. By THOMAS GRAY, B.Sc., F.R.S.E., and ANDREW GRAY, M.A., F.R.S.E., Assistant to the Professor of Natural Philosophy in the University of Glasgow, and J. J. DOBBIE, M.A., D.Sc. (Edin.), Assistant to the Professor of Chemistry in the University of Glasgow. Communicated by Professor Sir WILLIAM THOMSON, F.R.S. Received March 29, 1884.

The relation between the composition of glass and its electrical qualities has been studied by only a few experimenters, and our knowledge of the subject is still comparatively small. With regard to resistance to electrical conduction through its substance, Dr. Hopkinson has found among other interesting results, that potash or soda-lime glasses have a higher conductivity than flint glasses either light or dense; and his results as to electrical resistance confirm those given below.*

That the presence of a large quantity of alkali in glass is detrimental to its resisting quality has also been pointed out by Ekman.† In two papers ("Phil. Mag.," vol. 10, 1880, and "Proc. Roy. Soc.," vol. 34, p. 199), by one of the authors of the present paper, results are given of experiments on the variation of the resistance of glass of different kinds with temperature, and, more particularly in the second paper, with density and chemical composition.

It was inferred from the results of the electrical measurements

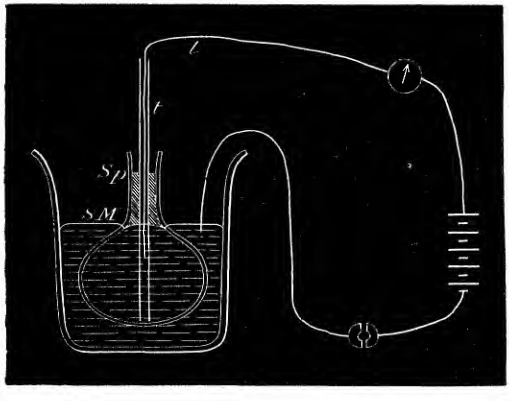
* "Phil. Trans.," vol. 167.

† "Phil. Mag.," vol. 40, 1870.

described in the second paper referred to, and the chemical analyses of the specimens experimented on, that in the case of flint glass, the electrical resistance increased with the density, and on the other hand that for potash or soda-lime glass, the resistance increased as the glass seemed to approach in composition to a definite chemical compound. Density, chemical composition, and resistance appeared all to be so related to one another in the case of the flint glasses experimented on, that increase of density, as well as approach to definiteness of composition, gave increase of resistance.

We offer the present paper as a contribution towards the further elucidation of this question. The experiments which are here described were carried out on glasses which differed considerably from those previously used. They were all flint glasses of considerable density, and it will be seen that though they differ widely in specific resistance, not one can be called a bad glass for electrical purposes. No experiments were made on potash and soda-lime glasses, as these are generally low in resistance, and our first object was to obtain definite information regarding comparatively dense glasses which former experiments show to be relatively much better insulators. It is our intention, however, in a continuation of the present research, to experiment both as to resistance and specific inductive capacity on lime glasses of varying composition.

FIG. 1.



The density of each specimen was carefully determined, and a complete chemical analysis made. The electrical experiments were made in the physical laboratory of the University of Glasgow, and the same general plan was followed as described in the paper mentioned above ("Proc. Roy. Soc.," vol. 34, p. 199). The arrangement of apparatus, with the exception of reversing key, &c.,

is shown in the accompanying drawing, fig. 1, which is taken from the previous paper. The glass which in each case was in the form of a small globular flask of about 7 centims. diameter, and from 2 to 3 millims. thick, was filled up to nearly the bottom of the neck with mercury, and immersed to the same level in mercury contained in an outer vessel. This outer vessel was contained in a sand-bath, which could be heated by means of a Bunsen burner placed below. The flask had in each case a neck several inches long, and one extremity of a wire l was passed down the neck so as to dip into the mercury within, while the other was connected through a sensitive galvanometer with a battery of about one hundred Daniell's cells. The other terminal of the battery was connected with the mercury in the outer vessel. To enable the current to be readily reversed, which was done between every successive pair of readings, a reversing key (not shown in the drawing) of somewhat novel construction, and of high insulation, was placed in the galvanometer stand and interposed in the wires joining the battery with the apparatus. It consisted simply of four slender pillars of vulcanite attached to a base piece of the same material. The top of each pillar was thicker than the stem, and had a hollow scooped out of it to receive mercury. In one side of the cup thus made, a piece of copper wire was fixed so as to terminate at one end in the interior of the cup, and at the other to give a projecting piece to which the battery wire could be attached. The hollows were filled with mercury and cross-bridges of copper wire used to connect the cups directly or diagonally, so as to give a current in one direction or the other as required.

The galvanometer used was the instrument described in the "Proc. Roy. Soc." vol. 36, p. 287, to which we refer for a full description, but the following brief account of the instrument may be conveniently given here. It consists of two pairs of coils with hollow cores arranged so that the axes of each pair are parallel and in a vertical plane. The coils act on a needle system of two horseshoe magnets of thin steel wire connected by a very light frame of aluminium, and hung with their planes vertical, so that a horseshoe corresponds to each pair of coils, and has its poles within the hollow cores. Each pair of coils is in this instrument carried by a brass plate, and these plates are set so as to make an angle with one another of about 106°. The needles are not plane, but curved round so as each to lie nearly in a cylindrical surface, the axis of which is the suspension fibre, and which passes through the cores of the coils without touching the coils on either side. Thus the needles can move in the hollow cores through considerable displacements without danger of coming into contact with the coils, and the cores are made smaller than would be otherwise possible. The needles enter the

coils from the same side, and the current is usually sent through the coils, so that one pair cause their horseshoe to move outwards, and the other pair their horseshoe to move inwards, thus turning the needle system round the suspension fibre. This system of needles when rightly adjusted is practically astatic in a magnetic field of uniform intensity. A magnet moved in azimuth by a tangent screw, and vertically by sliding along the vertical supporting rod, is used to give a difference of intensity to the magnetic field at the upper and lower ends of the needles, which are placed with similar poles turned in dissimilar directions.

The instrument is fitted with a distributing plate, the construction of which is fully described in the paper. By means of this plate the coils can be joined in series or in multiple arc, or in any possible combination of these modes of arrangement, so as to give all possible variations of resistance and sensibility, or can be arranged for use as a differential galvanometer when required.

The resistance of the coils when joined in series is slightly over 30,000 ohms, and it can easily be arranged to have a sensibility such as to give, when placed in series with a resistance of 10^{11} ohms in the circuit of a single Daniell's cell, a deflection of one division on a scale placed at a distance of a metre from the mirror. The instrument can easily be made still more sensitive, but when this is done the long period of the needle system renders it difficult to take readings quickly. This disadvantage may, however, be in great measure obviated by using a vane wholly immersed in liquid, or contained in a nearly closed air-vessel of proper size.

With a considerably less degree of sensibility we have found the instrument very convenient for the measurements described below. These were conducted in the following manner. The flask was heated by the sand-bath to a temperature above 100° C., and readings were then taken of the current sent through the glass when the battery was applied by means of the key. That the current measured by the galvanometer might not be affected by leakage through the table and other supports of the apparatus, the wire connected to the inside mercury coating of the flask was carried through air only direct to the galvanometer terminal, and tests were made as to whether the whole current shown by the galvanometer actually passed through the glass by withdrawing the connecting wire from the mercury inside the flask and bringing it into contact with the neck of the flask outside by twisting it round the glass. Such tests always showed that no leakage current existed, and that the current measured was really that passing through the substance of the glass from one mercury coating to the other. After a reading of the galvanometer in one direction had been obtained and recorded, with the temperature of the glass when the reading was taken, the

coatings of the flask were connected together until the next reading was about to be taken. For this reading the current was reversed and the deflection taken with its corresponding temperature, and so on throughout the series of observations in any particular case. The electrification was thus reversed between every pair of readings, and lasted in most cases three minutes. The resistances given below are, therefore, those after three minutes' electrification. The constant of the galvanometer for the battery used was determined once or twice in the course of each day's experiments, so that the resistance of the glass might be easily determined in absolute measure from the known thickness and surface of the flask. These were determined by weighing the flask, first empty in air, then with the globular part filled with water, then when immersed in water to a level a little above the former, to allow for the glass wanting on account of the orifice of the neck. The difference between the first and second weighings gave the capacity of the globe, from which its internal diameter on the supposition of sphericity could be calculated. The difference between the second and third weighings gave the volume of the globe from which, as before, the external diameter, and therefore the thickness of the glass, could be deduced. The resistances were then calculated for each specimen and multiplied by the mean surface in square centimetres and divided by the thickness of the flask in centimetres, so as to give the resistance between two opposite sides of a centimetre cube of the glass in question.

With regard to the results obtained at different temperatures, we have only to say that they confirm the conclusion formerly arrived at, that the conductivity of glass is doubled for every 8·5 or 9 degrees Centigrade rise of temperature. As, however, the object of the present experiments was mainly to further investigate the relation between resistance and chemical composition, they were not made through any very great range of temperatures.

In the following table we give the resistance, density, and chemical composition of each of the specimens experimented on and analysed. We give also results for one or two specimens, the electrical resistance and density of which were determined, but which were not analysed.

The general conclusion from a comparison of these data is, that the specific resistance of the glasses increases with the percentage of oxide of lead, and also with the density. With the exception of the glass marked XX, all the specimens which have been analysed follow the former law, and, with the exception of X and XX, also the latter law, as II, I, and III have practically the same density. But the two flasks X and XX seem anomalous in other respects. They contain for one thing a large quantity of lime as compared with the others, and this, no doubt, tends to diminish their resistance. The density of X

Mark on specimen.	Density.	Specific resistance in ohms.	Chemical composition.								Notes.
			Silica.	Lead oxide.	Lime.	Magnesia.	Oxide of iron, alumina, and manganese.	Potash.	Soda.	Total percentage.	
II	3·141	8400×10^{10}	47·544	40·557	0·250	0·144	1·750	7·598	2·157	100·0	Contains trace of manganese. Silica by diff. Contains 1·05 per cent. Fe_2O_3 equal to 0·945FeO.
IV	3·144	7250 „									
VII*	3·239	6960 „	..	33·85							
I	3·145	4700 „	55·700	37·098	0·336	0·014	2·500	3·080	1·420	100·148	Trace of manganese.
III	3·141	3868 „	50·104	36·987	0·224	0·198	1·950	8·837	1·700	100·0	Large trace of Mn. Silica by diff. Contains 1·4 per cent. Fe_2O_3 equal to 1·26FeO.
VI	2·854	534 „	62·686	20·606	0·672	0·270	2·00	11·610	2·156	100·0	Silica by diff. Trace of Mn.
V	2·811	453 „	62·263	19·877	0·616	0·216	2·20	11·944	2·884	100·0	Silica by diff. Trace of Mn. Contains 1·5 per cent. Fe_2O_3 equal to 1·035FeO.
X	3·018	545 „	57·50	17·882	2·660	0·360	5·700	8·910	6·838	99·85	Contains 1·2 per cent. of MnO; 3·5 per cent. Al_2O_3; 1 per cent. Fe_2O_3 equal to ·9FeO.
XX	2·829	85 „	58·85	21·423	2·622	0·288	3·357	7·899	5·933	100·372	Contains ·757 per cent. of MnO; 2·1 per cent. Al_2O_3; ·5 of Fe_2O_3 equal to ·45FeO.

* The percentage of lead oxide only was determined for this glass. It was not further analysed.

seems high when the quantity of lead oxide is considered, while the density of XX seems low for the same reason. Also comparing X with XX, we see that while XX contains more lead than X, and at the same time less of impurity, XX has a considerably lower density and a much lower specific resistance. The determinations of density and resistance were repeated for XX, and the results found practically to agree with those previously obtained. It may be interesting to note that, while all the others were new glasses, X and XX were glasses at least ten years old, which had been made for Sir William Thomson's experiments on the preservation of electric charges for a long time in hermetically sealed glass vessels.

The flask marked VII has a somewhat lower percentage of lead oxide than any one of the other glasses which are similar in resisting quality, but it will be noticed that its density is the highest of all. Only a determination of density and of the percentage of lead have been made for this glass. In the case of No. IV, the resistance was determined, but no analysis was made. We ought to state that I, II, III, IV, were all made by Messrs. Osler, Birmingham, and were understood to be from the same pot of glass.

Referring to the table on page 493, and considering the relation of the observed resistances to the amount of soda contained in the glass, we see that, except II and the anomalous glass XX, the resistances decrease as the percentage of soda increases; and making the same comparison for the percentages of potash, we find approximately the same kind of variation of resistance. This seems to indicate that, if other things were equal, the resistances would be diminished by increasing the proportion of alkali, a result which agrees with previous observations. We do not, however, consider the effect of alkali to be so important as the opposite effect of lead oxide.

In the paper referred to above ("Proc. Roy. Soc.," vol. 34, p. 199) it is stated that a glass which seems to approach in composition to a definite chemical compound is also good in point of resistance. It seems possible that in the case of those glasses which have approximately the same composition but different densities, those having the higher densities may approach more nearly to definiteness of composition. At all events, it is well known that minerals, more or less resembling glass in composition, which crystallise, have a greater density than substances of similar composition which are non-crystalline.

It will be seen that the glasses which we have experimented on differ very widely from those analysed by Dr. Divers. Although it is impossible to say in what proportion the silica is distributed among the bases, it may be useful to give the number of combining proportions of the oxides present in the various glasses, and the simplest formulæ which can be deduced from the analyses.

Specimen I.

This glass contains (eliminating traces of lime and magnesia)

$$80SiO_2.15PbO.3K_2O.2Na_2O,$$

or with the qualification which applies in all the cases below, that there is nothing to indicate the manner in which the silica is distributed among the bases,

$$3\{3(PbO.4SiO_2)+(K_2O.4SiO_2)\}+2\{3(PbO.4SiO_2)+(Na_2O.4SiO_2)\}$$

	Found.		Calculated.
SiO_2	57·25		56·6
PbO	38·13		38·57
K_2O	3·16		3·25
Na_2O	1·45		1·43
	99·99		99·85

Specimen II.

$$22SiO_2.5PbO.2K_2O.Na_2O,$$

with elimination of traces of lime and magnesia; or

$$2\{5(PbO.2SiO_2)+3(K_2O.4SiO_2)\}+\{5(PbO.2SiO_2)+3(Na_2O.4SiO_2)\}$$

	Found.		Calculated.
SiO_2	48·56		49·15
PbO	41·44		41·52
K_2O	7·76		7·01
Na_2O	2·25		2·31
	100·01		99·99

Specimen III.

$$61SiO_2.12PbO.7K_2O.2Na_2O;$$

or,

$$7\{2(K_2O.3SiO_2)+3(PbO.3SiO_2)\}+2\{2(Na_2O.3SiO_2)+3(PbO.3SiO_2)\}$$

	Found.		Calculated.
SiO_2	51·32		51·63
PbO	37·88		38·31
K_2O	9·05		8·40
Na_2O	1·74		1·58
	99·99		99·92

It is curious to note that this glass agrees very closely in composi-

tion with a crystal glass analysed by Berthier, to which he assigns the formula—

$$2(K_2O.3SiO_2)+3(PbO.3SiO_2).$$

Specimen V.

$$2PbO.3K_2O.Na_2O.24SiO_2;$$

or,

$$3\{(PbO.2SiO_2)+2(K_2O.5SiO_2)\}+\{PbO.2SiO_2)+2(Na_2O.5SiO_2)\}$$

	Found.		Calculated.
SiO_2	64·21		64·55
PbO	20·50		20·0
K_2O	12·31		12·66
Na_2O	2·97		2·77

Specimen VI.

This flask has obviously the same composition as V.

Specimen X.

Eliminating the lime and trace of magnesia, we have as expressing the composition of this glass—

$$4PbO.5K_2O.5Na_2O.48SiO_2;$$

or, $$\{2(PbO.2SiO_2)+5(K_2O.4SiO_2)\},$$

mixed with $$\{2(PbO.2SiO_2)+5(Na_2O.4SiO_2)\}$$

	Found.		Calculated.
SiO_2	63·09		63·29
PbO	19·62		19·59
K_2O	9·77		10·34
Na_2O	7·5		6·8
	99·98		100·02

Specimen XX.

$$PbO.K_2O\ Na_2O.10SiO_2;$$

or, $$\{(PbO.2SiO_2)+2(K_2O.4SiO_2)\}$$

mixed with $$\{(PbO.2SiO_2)+2(Na_2O.4SiO_2)\}$$

	Found.		Calculated.
SiO_2	62·5		61·28
PbO	22·76		22·77
K_2O	8·33		9·62
Na_2O	6·3		6·33
	99·89		100·00

It is curious to notice with regard to XX, which is anomalous in most respects, that it gives a chemical formula widely different from that found for X.

We had hoped to be able to include the results of experiments on the resistances of crystals and minerals. Several sections of different substances have been made, and some of these have been already analysed. Among them are a plate of quartz, cut parallel to the principal axis, and a plate cut parallel to the secondary axes of the crystals, and by means of these specimens we propose to endeavour to find the resistance and specific inductive capacity in different directions relatively to the crystallographic axes. The electrical experiments are not yet, however, completed, but we hope soon to overtake the work.

As the surface of these sections is small, we propose to use the electrometric method by loss of charge, and to eliminate the capacity of the condenser formed by the substance under examination and the electrometer, by using a sliding cylindrical air-condenser, which will allow us to vary the capacity by a known amount.

Our proposed experiments on the specific inductivities of different kinds of glass have been delayed principally for want of a standard air-condenser. We propose, however, now to use an air-condenser, the capacity of which can be altered by a known amount, and Sir William Tomson has very kindly placed at our disposal for this purpose his sliding air-condenser. As soon as Sir William Thomson's standard spherical condenser, which is at present on loan, is returned to the laboratory, we shall be able to verify the results to any necessary extent by comparison.

It was at first our intention to employ the method of electric oscillations used by Schiller* in his experiments on the specific inductive capacity of different substances, but for various reasons we have decided to employ a different method. In the ordinary theory of the oscillatory discharge of a condenser through a coil of large self-induction, it is assumed that the current at any instant has the same strength throughout the whole length of wire in the coil. Now, although this is no doubt approximately true when the coil connects the plates of a condenser of great capacity, it cannot, on account of the considerable electrostatic capacity of the coil itself (a capacity which, taken per unit length of the wire, must vary along the wire in a manner which, so far as we know, has not yet been worked out) be true when the capacity of the discharging condenser is small in comparison with that of the coil.† On this theoretical ground, and also because of the somewhat elaborate and delicate apparatus for measuring very small

* Schiller, "Pogg. Ann.," 1874.

† "On the True and False Discharge of a Coiled Electric Cable," by Professors Thomson and Fleeming Jenkin, "Phil. Mag.," September, 1861; or "Mathematical and Physical Papers," by Sir William Thomson, Art. LXXXIII.

intervals of time which the method renders necessary, we decided, after all our apparatus and arrangements had been planned, to adopt some other method, and we are indebted to Sir William Thomson for the suggestion of a method which promises to be at once easy and likely to give results nearly or altogether independent of "electrification," and we have made arrangements for using it in our continued experiments. One plate of an air-condenser, the capacity of which is known, is joined to the upper end of a fine wire which forms the thread of a pendulum, of which a small metal ball is the bob. Another exactly similar pendulum has, connected to the upper end of its wire, one plate of the experimental condenser, while the other two plates of the condensers are connected to the case of an electrometer used to measure the potential to which the air-condenser is charged. Supposing the air-condenser to be charged, and its potential measured by means of the electrometer, and the experimental condenser to be uncharged, the ball connected with either condenser is drawn aside, and let go so as to fall against the other ball. The balls being of an equal size and of the same material, the first ball will be brought to rest, and the other ball will immediately be set into motion, the time of contact being very short and capable of being approximately estimated. The second ball is caught, and prevented from returning. The charge of the air-condenser has been shared by the contact with the experimental condenser, and the diminution of potential is read off by the electrometer, and from the result the specific inductive capacity of the material forming the experimental condenser can be found; and, as the time of contact is very short, the result will be but very slightly, if at all, influenced by "electrification." We may easily arrange, in ways which we need not here point to, this method for use as a null method.

We propose in a continuation of our experiments to eliminate the uncertainty which still exists as to the effect of impurities in the glass, and to test the effect of varying the proportions of the ingredients, and of adding impurities by making up glasses from pure chemicals. The results of experiments, such as those described above, are so complicated by the presence of small quantities of what may be called "foreign" ingredients, that it seems unlikely that more definite results than those already obtained can be expected as to the exact relation between composition and resistance unless such experiments as we propose be made.

We are also extending our experiments to crystals of quartz, felspar, and other minerals, and to natural glasses, and further to glasses produced by melting natural crystals which are capable of assuming the vitreous condition. We hope to obtain results as to the relation of electrical quality to the crystallographic axes of the crystal.

FIG. 1.